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6. AUTHOR(S) Anshel Gorokhovskiy					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Engineering Science and Physics, The College of Staten Island, 2800 Victory Blvd., Staten Island, NY 10314				8. PERFORMING ORGANIZATION REPORT NUMBER Final Technical Report	
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13. ABSTRACT (Maximum 200 Words)  Over the report period, an optical laboratory for characterization materials for frequency domain optical storage was upgraded. A practical approach for the determination of the quantum efficiency of persistent spectral hole burning using dispersive kinetics was developed. The optical properties of several $Tm^{3+}$ chelates complexes were studied. Optical absorption, steady state photoluminescence, and persistent spectral holes at the $^3H_6(1) \leftrightarrow ^3H_4(1)$ transition near 800 nm were studied within broad temperature range. Persistent spectral holes were detected at temperature between 1.5 and 20 K. Holes burning and refilling mechanisms were analyzed. A photoluminescence of five natural diamonds (type Ia) implanted with Xe ions with dose range $1 \times 10^{13} - 5 \times 10^{14} \text{ cm}^{-2}$ was investigated as a function of thermal annealing at temperatures between 300 and 1400 C. A narrow zero-phonon line at 813.7 nm (1.523 eV) was observed for all samples. As the annealing temperatures was increasing from 800 to 1400 C, the luminescence at 813.7 nm gradually amplified in all four samples with rate depending on the ion implantation dose					
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**Spectroscopic Studies of Materials for Spectral Hole Burning Optical Storage**

March 14, 2002

Principal Investigator: Prof. Anshel Gorokhovsky

Ph.D. Graduate Students: Mr. Alex Turukhin

Ms. Agnes Carpenter

Mr. Ting-Yi Chu

Mr. Brian Collins

Undergraduate Student: Mr. Alexander Vaysman

Collaborators: Prof. Y. Okamoto, Chemistry Department,

Polytechnic University, Brooklyn, NY

Dr. A. M. Zaitsev, University of Hagen, Germany

Materials are one of the key elements to advance the spectral hole-burning (SHB) technology for optical storage and processing. Our research is directed to evaluation of some prospective materials for optical hole-burning frequency and time-domain storage applications. Goal of our project is to provide research training for Ph.D. and undergraduate students in the field of optical spectroscopy of materials for optical hole-burning frequency and time-domain storage applications.

Major focus was on investigation of several thulium ions doped polymers and on optical characterization of some doped and ion implanted diamonds as actual materials. Diamond is a covalent, extremely hard and highly thermoconducting carbon crystal. Due to its extreme hardness, diamond has a very high Debye temperature  $T_D \approx 2000$  K. Therefore, diamond may be a prospective material for high-temperature PHB storage. Our interest to  $Tm^{3+}$  doped metallo-organic materials is motivated by the need to combine unique properties of the rare-earth ion (weak electron-phonon interaction, long coherence time) with the ability of the organic surrounding to change its local structure under laser excitation of the rare-earth ion. The latter may serve as a persistent hole-burning mechanism for multi-frequency optical storage. The  $Tm^{3+}$  ion is especially of interest because the transition between the  $^3H_6(1)$  and the  $^3H_4(1)$  crystal field levels occurs in the region of GaAlAs diode lasers near 800 nm, which is clearly advantageous for possible technological applications. To characterize and compare different potential hole burning materials, we determined some material parameters including excited state optical lifetime, inhomogeneous linewidth, homogeneous holewidth, hole lifetime, persistent hole annealing temperature, and some others. Special attention was paid to the determination of the quantum yield of hole-burning materials.

Over the report period the progress was achieved in areas of upgrading of laboratory equipment and research.

### **1. Laboratory**

Equipment in our laser and optical spectroscopy laboratory was upgraded to perform spectroscopic research and to characterize hole-burning materials. Major spectroscopic equipment including Perkin Elmer Lambda 900 UV/VIS/NIR Spectrophotometer and the high-

resolution double spectrometer Spex 1404 has been purchased and installed. A new Oxford Instruments variable temperature helium cryostat has been purchased and helium pump and pumping line have been installed. This unit allows us to perform measurements at temperatures from 1.4 to 300 K with low level of mechanical vibrations. Hole burning measurements were made with a tunable single frequency CW Ti-sapphire laser (Coherent 899-29). The laser intensity was stabilized at the level of 0.1 %. Detection system consists of lock-in amplifier, monochromator, GaAs cooled photomultiplier, and computer data acquisition board.

A simple optical method for studying mechanical vibrations has been developed and applied to investigation of commercial closed cycle refrigeration system CRYO Model 396-022. The method is based on amplitude modulation of laser beam intensity by a knife-edge mounted on the sample holder. The sensitivity of this optical technique is determined by the diameter of the focused beam, and the sensitivity of 1  $\mu\text{m}$  is readily achievable. A Fourier transform was used to analyze the vibration spectrum. Studies were conducted for different temperatures, orientations, and mechanical holders. The amplitudes of the vibrations were on the order of a 50  $\mu\text{m}$ . The drive motor of the cold head produced strong vibrations at 60 Hz and 120 Hz, while the piston generated major vibrations at 3 Hz. To minimize sample vibrations, a special cold head support was developed. This support allowed us to use this refrigeration system in conjunction with Lambda 900 spectrophotometer for low temperature absorption spectroscopy. However, optical storage applications require additional vibration decoupling interface.

## **2. Research.**

### **2.1 Rare earth doped polymers.**

Several  $\text{Tm}^{3+}$  doped polymers have produced for our study (Prof. Y. Okamoto, Mr. Ting-Yi Chu). Samples under investigation were the  $\text{Tm}^{3+}$  ion complexes formed using thulium chloride ( $\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$ ) with thenoyltrifluoroacetylacetone [TTFA], 1,1,1-trifluoro-2, 4-pentanedione [TFD], 1-phenyl-1, 3-butanedione [PBD] and 1,3-diphenyl-1, 3-propanedione [DBM] ligands in poly (methyl methacrylate) matrix.

Optical absorption, steady state and time-resolved photoluminescence, and spectral hole burning at the transition between the  $^3\text{H}_6(1)$  and the  $^3\text{H}_4(1)$  crystal-field levels, were studied at

temperatures between 1.4 and 300 K. To determine the magnitude of inhomogeneous broadening, an absorption band was numerically fitted by the superposition of a few Gaussians. The width of the Gaussian centered at the transition between the lowest crystal field components,  ${}^3H_4(1) \leftarrow {}^3H_6(1)$ , gives the inhomogeneous broadening of this transition and was found to be between 90 and 140  $\text{cm}^{-1}$  for different complexes. In addition, the fitting allowed us to determine the crystal field splitting of the  ${}^3H_4$ , as well as  ${}^3H_6$  ground state for each complex.

Luminescence spectra of the  $\text{Tm}^{3+}$ -ligand complexes were investigated in the region of the  ${}^3H_4 \rightarrow {}^3H_6$  transition in the wavelength range between 750 and 850 nm. The  ${}^3H_4 \rightarrow {}^3H_6$  and  ${}^1G_4 \rightarrow {}^3H_5$  luminescence decays, as well as the background emission decays, were also measured in the different materials after  ${}^1G_4 \leftarrow {}^3H_6$  pulsed excitation at 476.5 nm for  $T = 1.4$  K. The luminescence quantum yield was estimated on the bases of relative luminescence intensity, absorption at the laser wavelength, and level lifetime.

Optical spectral hole burning was investigated at different temperatures. Persistent spectral holes were detected in all materials at temperatures between 1.4 K and 20 K. Spectral holes show no visible recovery at 1.4 K over the experimental time of 10 hours. The maximum measured hole depth was about 50 %. No side band structure was observed. The hole-burning mechanism appears to be a photoinduced rearrangement of the local structure. The holewidth dependence on burning time at different intensities was used to determine the conditions for the weak burning intensity regime. The "true" holewidths for different materials were found to be  $\Gamma_{\text{hole}} = 180\text{-}360$  MHz by using the zero limit of the burning intensity and of the exposure time. Spectral hole widths show weak power law temperature dependence  $T^n$  with  $n = 1\text{-}1.6$ . To verify the ability of the materials under investigation to store a number of spectral holes, we performed hole burning at different wavelengths over the inhomogeneously broadened absorption band. Holes were observed over the full inhomogeneously broadened band of the  ${}^3H_6(1) \rightarrow {}^3H_4(1)$  transition, i.e. in the bandwidth of 100  $\text{cm}^{-1}$ , or 3000 GHz. No visible laser - induced filling or broadening was detected. The results on inhomogeneous and hole width are collected in the Table.

**Table.** Holewidths and inhomogeneous widths of the  $^3\text{H}_4 (1) \leftarrow ^3\text{H}_6 (1)$  transition of  $\text{Tm}^{3+}$  chelates in PMMA.

Parameters	$\text{Tm}(\text{TTFA})_3$	$\text{Tm}(\text{TFD})_3$	$\text{Tm}(\text{PBD})_3$	$\text{Tm}(\text{DBM})_3$
$\Gamma_{\text{inh}}$ (GHz)	3000	4300	2800	2500
$\Gamma_{\text{hole}}$ (MHz)	220	230	360	180
$\Gamma_{\text{inh}} / \Gamma_{\text{hole}}$	$1.4 \times 10^4$	$1.9 \times 10^4$	$0.8 \times 10^4$	$1.4 \times 10^4$
$n (\Gamma_{\text{hole}} \sim T^n)$	$1.6 \pm 0.15$	$1.3 \pm 0.15$	$1.0 \pm 0.15$	$1.5 \pm 0.15$

To analyze a hole profile, we measured the hole several times at close frequencies and accumulated the spectra. The typical profile observed in all materials was non-Lorentzian. The hole shape was best described by the superposition of two Lorentzians. The dependence of the hole shape upon wavelength position within the inhomogeneous band between 789 nm and 798 nm was studied. An interesting trend was found: while widths of the constituted Lorentzians remain practically constant across the spectral range studied, the ratio of their amplitudes was changing. The widths of the constituted holes were found to be  $230 \pm 20$  MHz and  $1.3 \pm 0.2$  GHz. The observed results may be explained by the existence of two unresolved overlapping spectral components inside the inhomogeneous absorption band. In this case, the observed spectral hole is a superposition of two independent holes, broad and narrow, with holewidths remaining approximately constant across the inhomogeneous band. Fitting the experimental dependence, the widths of the hidden inhomogeneous components were found to be 5.6 nm and 4.6 nm, respectively and the peak wavelengths close to 793.9 nm for both components. These components most likely originate from two different sites of the  $\text{Tm}^{3+}(\text{TTFA})_3$  in PMMA having different dephasing rates. These rates are reflected in different widths of the constituted holes. Due to the complex shape of the spectral holes, the holewidth reported above refers to the “effective” holewidth measured at half amplitude.

Kinetics of the spectral hole burning were recorded at time scale of  $10^{-2}$  -  $10^4$  s. They showed dispersive behavior associated with random structure of the  $\text{Tm}^{3+}$  ion surrounding. Analyze of the dispersive kinetics allows to determine the quantum efficiency of SHB. Average quantum efficiency was found to be in range  $10^{-6}$  to  $10^{-4}$  and was related to the chemical structure of samples studied. Hole burning and refilling mechanisms were analyzed in the frame of ion interaction with two-level low-frequency excitations. The energy barrier between the

photoproduct and educt states for the  $\text{Tm}^{3+} (\text{TTFA})_3$  complex was determined from hole area temperature cycling to be on the order of  $700 \text{ cm}^{-1}$ . This value corresponds to the maximum annealing temperature  $T_{\text{Amax}} = 20 \text{ K}$  for  $\text{Tm}^{3+} (\text{TTFA})_3$  and about 30% of the initial hole area conservation at our experimental conditions. The maximum annealing temperature was determined for all complexes, and its correlation with the size of the side groups was established. A likely mechanism of the hole filling after temperature cycling is a thermally activated rotational displacement of the ligand side groups. A dramatic decrease of quantum efficiency with increasing temperature was observed and analyzed in terms of activation and quantum tunneling processes.

Spectroscopic results indicate glass-like properties for these materials, i.e. a high degree of disorder in the  $\text{Tm}^{3+}$  coordination surroundings. The materials have large inhomogeneous broadening, and merit further investigation for possible hole burning frequency- and time-domain storage and other applications.

**2.2 Ion Implanted Diamonds.** Our project is mostly focused on optical characterization of some ion implanted natural diamonds as actual materials. These systems are outstanding materials due to their extreme hardness, have high frequency phonon spectra and dip electron traps. Therefore, they are good potential materials for high temperature, and non-volatile optical storage. We continued photoluminescence study of natural diamonds containing Xe impurity centers with zero phonon line at  $813.7 \text{ nm}$  ( $1.523 \text{ eV}$ ). Photoluminescence measurements have been performed at temperatures  $1.3 - 300 \text{ K}$ . Samples under investigation were five natural diamonds (type Ia) irradiated with  $500 \text{ keV}$  Xe ions at room temperature over dose range  $1 \times 10^{13} - 5 \times 10^{14} \text{ cm}^{-2}$ . A sample with dose of  $5 \times 10^{14} \text{ cm}^{-2}$  was subsequently thermally annealed at  $1400 \text{ C}$  for 2 hours and served as the control sample. This sample has the highest intensity of line at  $813.7 \text{ nm}$ . Another four sample were annealed gradually (Dr. A.M. Zaitsev) at temperatures between  $300 \text{ C}$  and  $1300 \text{ C}$  with increment of  $100 \text{ C}$ . Subsequent photoluminescence measurements were performed after each annealing cycle to investigate process of activation of Xe centers. No luminescence was observed at temperatures less than  $800 \text{ C}$ . As the annealing temperatures was increasing from  $800$  to  $1400 \text{ C}$ , the luminescence at  $813.7 \text{ nm}$  gradually amplified in all four

samples. The most significant growth (about 25 times) was observed for sample with the list Xe ion implantation dose. This behavior may be explained by significance of nonradiative photoluminescence quenching in the most heavily implanted, and therefore, the most damaged samples. Further thermal annealing at 1500 C will be performed and photoluminescence and hole burning will be studied. Width of the zero-phonon line at 1.4 K was determined to be of  $10 \text{ cm}^{-1}$ . A weak phonon band was observed in the wavelength region 815 - 840 nm. This material is potentially interesting for high temperature optical storage and its investigation will continue.

#### **Publications and presentations:**

- A. V. Turukhin and A. A. Gorokhovsky, "Temperature Dependent Photophysical Hole Burning in Thulium Doped Polymers" Presented at the 7<sup>th</sup> International Meeting on Hole Burning, Single Molecule and related Spectroscopies: Science and Applications, Taipei, Taiwan, ROC, November 18-23, 2001, p13.
- A. V. Turukhin, A. V. Carpenter, A. A. Gorokhovsky, T. Chu and Y. Okamoto, "Hole Burning Spectroscopy of Thulium Chelates", *J. of Luminescence* **86**, 333 (2000)
- A. V. Turukhin and A. A. Gorokhovsky, "Determination of quantum efficiency of persistent spectral hole burning using dispersive kinetics", *Chem. Phys. Lett.* **317**, 109 (2000).
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- A. V. Turukhin, A. V. Carpenter, A. A. Gorokhovsky, R. R. Alfano, T. Chu, and Y. Okamoto, "Optical spectroscopy of  $\text{Tm}^{3+}$  in organic matrices for hole-burning storage applications", *Proc. of the SPIE's 43rd Annual Meeting*, San Diego, CA, July 19 - 24, 1998, **Vol. 3468**.
- A. V. Turukhin, A. A. Vaysman, and A. A. Gorokhovsky, "Evaluation of vibration generated by closed cycle refrigeration system using optical methods", *Proc. of the SPIE's 43rd Annual Meeting*, San Diego, CA, July 19 - 24, 1998, **Vol. 3435**.
- A. A. Gorokhovsky, A. V. Turukhin, A. V. Carpenter, R. R. Alfano, T. Chu, and Y. Okamoto, "Optical spectroscopy of  $\text{Tm}^{3+}$ : ligand complexes for hole-burning storage applications", Presented at the International Symposium on Optical Science, Engineering, and Instrumentation, SPIE's 43rd Annual Meeting, San Diego, CA, July 19 - 24, 1998, Conference 3468.
- A. V. Turukhin, A. A. Vaysman, A. A. Gorokhovsky, "Evaluation of vibrations generated by closed cycle refrigeration system using optical methods", Presented at the International Symposium on Optical Science, Engineering, and Instrumentation, SPIE's 43rd Annual Meeting, San Diego, CA, July 19 - 24, 1998, Conference 3435.